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Revision 0

On the Anodic Polarization Behavior of Carbon Steel in Hanford Nuclear Wastes

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

CH2MHILL
Hanford Group, Inc.

P.O. Box 1500
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ON THE ANODIC POLARIZATION BEHAVIOR OF CARBON STEEL IN HANFORD NUCLEAR WASTES

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ABSTRACT

The effect of the important chemical constituents in the Hanford nuclear waste simulant on the anodic behavior of carbon steel was studied. Specifically, the effect of pH, nitrite concentration, nitrite/nitrate concentration ratios, total organic carbon and the chloride concentration on the open circuit potential, pitting potential and repassivation potential was evaluated. It was found that pH adjusting, although capable of returning the tank chemistry back to specification, did not significantly reduce the corrosivity of the stimulant compared to the present condition. Nitrite was found to be a potent inhibitor for carbon steel. A critical concentration of approximately 1.2M appeared to be beneficial to increase the difference of repassivation potential and open circuit potential considerably and thus prevent pitting corrosion from occurring. No further benefit was gained when increasing nitrite concentration to a higher level. The organic compounds were found to be weak inhibitors in the absence of nitrite and the change of chloride from 0.05M to 0.2M did not alter the anodic behavior dramatically.

Key words: pitting, pH, nitrite, nitrate, TOC

INTRODUCTION

At the United States Department of Energy's Hanford tank reservation, the tanks contain approximately 50 million gallons of liquid legacy radioactive waste from cold war weapons production, which is stored in 177 underground storage tanks. Eventually the waste will be vitrified and the resulting waste glass logs will be disposed at the Yucca Mountain Repository. However, the double shelled carbon steel storage tanks presently used for storage will continue in operation until the vitrification plant construction is finalized and waste processing operations completed.

Generally, all of the wastes tend to be highly alkaline in nature, typically with pH values greater than 10 and to hydroxide concentrations in excess of 6M. However, the waste chemistry will tend to change over time due to various chemical reactions taking place inside the tanks. In addition, the present chemistries for some of the tank waste types are no longer in specification with respect to corrosion (e.g., maintaining pH levels above 13-13.5). With reference to Tank 241-AN-107, for example, the present pH is between 11 and 12 in comparison to the operational specification of greater than 13. Thus, there is concern within DOE and regulatory bodies that tank integrity will be compromised given these changes in chemistry. Furthermore, if tank integrity is potentially compromised, there is a need to define mitigation procedures.

A previous investigation showed that localized corrosion and stress corrosion cracking (SCC) were unlikely in the existing and expected composition of the waste¹. However, since these wastes are a complex mixture of nitrate, nitrite, organic compounds (e.g., acetate, oxalate, ethylenediaminetetraacetate, and glycolate), hydroxide, chloride, and other species the influence of each of these on possible tank performance is unclear. When separately present in other systems, most of these constituents have been studied individually to address their effects on localized corrosion of various materials^{2,3,4,5}. However, their effects on localized corrosion of carbon steel in a complicated radioactive waste are still unknown. The work performed by SRL and others on the nuclear waste did not systematically address the effect of the constituents listed above on the localized corrosion of carbon steel^{6,7}.

Thus, the objective of this work is to determine the range of conditions where the tank steel is susceptible to localized corrosion and thus to provide insights to define possible corrosion mitigation strategies the supernatant and sludge regions. Particularly, the effects of pH, nitrite concentration, organic compounds (i.e., the total organic carbon (TOC) level) on the electrochemical polarization behavior, characterized by OCP, pitting potential and repassivation potential, were studied. The effects of the chemical constituents on SCC were studied as well and the results are presented elsewhere^{8,9}.

EXPERIMENTAL APPROACH

Materials and Specimens

All test specimens were fabricated from three 91.4 cm × 61 cm × 2.54 cm (3'×2'×1") as-supplied plates of ASTM A537 Class 2 carbon steel material that had been heat-treated to obtain material properties similar to those of the Class 1 carbon steel used for construction of the double shell storage tanks. A schematic drawing of the specimen used in this work is shown in Figures 1. Specimens were fabricated by Metal Samples Company*. Material close to the flame cuts at the edges of the plates was avoided for specimen fabrication to ensure consistent microstructures.

Experimental Environment

A solution that was developed to stimulate the environment in the Tank 241-AN-107 (AN107 hereafter) was used in the present work. The detailed recipe can be found elsewhere⁸. Table 1 is a summary of the main constituents in the waste simulants. Other solutions were obtained based on the standard solution by adjusting the concentration of the chemical of interest (e.g., nitrite, nitrate, TOC and chloride). For each test, the solution was mixed 24 hours before starting the test so that the chemicals would dissolve completely. During this time period, the solution was kept on a constantly vibrating shaker to avoid any possible precipitation. The pH of the solution was adjusted shortly before the use of the solution with either sodium hydroxide or sulfuric acid depending on the desired final pH (the initial pH was between 10 and 11 before adjusting).

Open Circuit Potential and Cyclic Potentiodynamic Polarization Testing

Prior to CPP testing, the specimens were ultrasonically cleaned with isopropanol for five minutes, rinsed with deionized (DI) water, and then dried with nitrogen. For each test, the solution was purged with nitrogen for one hour while waiting for the temperature to reach 50°C (122°F) before the specimen was placed in the test solution. Prior to CPP testing, the open circuit potential (OCP) was monitored for 18 hours. Then the potential scan was started from -500 mV vs. saturated calomel reference electrode (SCE) with a scan rate of 0.17mV/s and reversed at +400 mV vs. SCE or when the current reached 1mA/cm², whichever occurred first. A platinum wire loop was used as the counter electrode. The solution was continuously purged with nitrogen throughout the test to maintain a deaerated condition.

When a CPP test was completed, the specimen was removed from the test solution, rinsed with DI water, and then dried with nitrogen. If excessive corrosion products were present on the specimen surface, the specimen was then ultrasonically cleaned in acetone for five minutes to remove the corrosion product. It was then rinsed with DI water and dried with nitrogen. The post-test appearance of the specimen was photographically documented to show the evidence of corrosion attack.

Potentiostatic Tests

* Munford, AL

The pitting and repassivation potentials can usually be determined by either CPP tests or potentiostatic tests. For the present work, the CPP test was performed first. In most cases, the pitting potentials were obtained directly from the CPP curve at the potential where current increased dramatically. If the CPP curve showed two slope changes on the forward scan in the transpassive region (e.g., Figure 2), then the potential where the second slope change occurred was selected as the pitting potential. Similarly, the repassivation potentials were obtained directly from the CPP curve at the zero current potential on the reversal scan. However, some CPP curves showed an inflection point on the reversal scan at a potential higher than the zero current potential, as shown at location (1) in Figure 2. Therefore, potentiostatic tests were performed for the solutions in which a definitive repassivation potential could not be determined directly from the CPP curve due to either the presence of the inflection point or a very negative zero current potential. In the former cases, the potentiostatic tests were performed at potentials selected to bracket the potential at the inflection point (i.e., at potentials lower and higher than point (1) in FIGURE 2). In the later cases, the potentiostatic tests were performed at potentials more positive than the zero current potential. For each potentiostatic test, the CPP test was first performed and the potential was scanned to the reversal potential, and then stopped on the back scan at the potential where the potentiostatic test would be performed. The test was such arranged that pits with depths comparable to those observed in the standard CPP tests would be initiated on the forward scan. Immediately after the CPP test, the potentiostatic test was started at the potential of interest and the current change as a function of time was monitored for a period of usually 24 hours or longer. Other testing conditions remained the same as used in the CPP tests. If the current was observed to increase with time, it indicated that the applied potential was more noble than repassivation potential. Conversely, if the current decreased with time or remained small, the indication was that the applied potential was below the repassivation potential. Each of these cases is illustrated in Figure 3.

RESULTS AND DISCUSSION

This section summarizes the results and key findings from the electrochemical tests (i.e., CPP and potentiostatic tests). The effects of pH, nitrite concentration, nitrite/nitrate ratio, total organic carbon (TOC) concentration and chloride concentration on the open circuit potential, pitting potential (E_{pit}) and repassivation potential (E_{rp}) are discussed.

Effect of Solution pH

The data in Figure 4 show that pH affected all three electrochemical parameters. The OCP decreased (move in the negative direction) from about -200 mV at pH 7 to -538 mV at pH 13.5. It is generally expected that the OCP will decrease with an increase of pH because the equilibrium potentials of the chemicals that have dominated cathodic reactions shift in the negative direction with an increase in pH. Thus, OCP will shift towards the negative direction according to mixed potential theory, assuming the pH shift did not have a significant impact on the anodic reaction. Figure 4 also shows that E_{pit} generally decreased with increasing pH whereas E_{rp} decreased from pH 7 to pH 9, but then dramatically increased from pH 9 to 11. With further increases in pH, E_{rp} again decreased.

The most important parameter from the standpoint of pit initiation is the difference between the repassivation potential (E_{rp}) and OCP, as well as the difference between the pitting potential (E_{pit}) and the repassivation potential (E_{rp}). This difference between E_{rp} and OCP is the safety margin when E_{rp} is used as a design parameter. In the environment of interest, this safety margin is extremely important since larger margins usually imply that the propensity and risk for localized corrosion is lower. The importance of this potential difference is further highlighted by the frequent observation that the OCP of many materials in different environments will tend to asymptotically increase (become more noble) with time until a nominally steady state value is reached.

Figure 5 shows that the difference between E_{pit} and E_{rp} , E_{rp} and OCP as a function of pH. Clearly, the differences were positive and relatively large for pH values above 10, indicating that pit initiation is relatively unlikely to occur at these elevated pH values. On the other hand, the E_{rp} value was extremely close to OCP at pH 7, indicating that pit initiation is much more likely to occur.

Figure 5 also shows that the difference between either E_{pit} and E_{rp} or E_{rp} and OCP did not change significantly above pH 11 with further increases in pH. From the perspective of pitting corrosion, this could imply that although the current chemistry in AN107 is out of specification with respect to pH (pH 11 rather than specified pH 13), the environment of interest appears to have no significant difference on corrosivity to carbon steel at pH 11 to pH 13 or higher. Thus, pH adjustment towards more alkaline conditions might not provide further benefits in terms of optimizing the tank operation conditions.

Effect of Nitrite and Nitrite/Nitrate Ratio

Nitrite was found to have a significant effect on the CPP curves, as shown in Figure 6. Basically, the CPP curves in AN107 solution with higher nitrite concentrations exhibited higher (more positive) pitting and repassivation potentials. The comparison of the specimen appearance in Figure 7 indicated that the pitting corrosion was less severe at higher nitrite concentration.

The effect of nitrite concentration on OCP, E_{pit} and E_{rp} is shown in Figure 8. Note that the values at 2.3M nitrite were obtained from AN107 endpoint solution at pH 10, which also had a lower nitrate concentration of 2.4M compared to other solutions (3.7M). When the nitrite concentration was zero, there was no real repassivation potential as the CPP curve did not close at any potential tested (i.e., no zero current potential was observed). In these cases, the final potential (-500 mV) was used as the repassivation potential.

Figure 8 shows that nitrite concentration appeared to have very little effect on the OCP. The more positive OCP value at 2.3M nitrite was likely due to the pH difference of that solution (i.e., endpoint solution). However, the effect of nitrite concentrations on E_{pit} and E_{rp} is evident. The values of E_{pit} and E_{rp} generally were more positive at higher nitrite concentrations. There appears to be a critical nitrite concentration (~ 1.2M) below which the repassivation potentials were more negative than OCP. Therefore, pitting corrosion could initiate at OCP under such conditions although the initiation could be significantly delayed. It can also be seen from Figure 8 that the repassivation potentials were closer to the pitting potentials at higher nitrite concentrations. This further demonstrates that nitrite appears to be a potent inhibitor for carbon steel in AN107 solutions since the smaller difference between E_{rp} and E_{pit} indicates better

pitting corrosion resistance of A537. However, no extra benefit with respect to improving the pitting and repassivation potentials was gained with further increases in the nitrite concentration above 3.5M. Based on the effect of nitrite on the repassivation potential, a critical nitrite concentration above 1.2M might be beneficial since the repassivation potential is significantly above OCP at this concentration. With further investigations, a link between the repassivation potential and hence the critical nitrite concentration and the occurrence of the SCC on carbon steel might be established. This is discussed elsewhere^{8,9}.

The standard AN107 simulant contains 1.2M nitrite and 3.7M nitrate. In the endpoint solution the nitrite was increased to 2.3M whereas nitrate was reduced to 2.4M. Therefore, the concentration ratio as well as the absolute concentrations of nitrite and nitrate is predicted to change with time. As discussed above, nitrite generally is beneficial to carbon steel in terms of improving the resistance to pitting corrosion in nitrate solutions. However, it was not clear whether the positive movements in the pitting potential and the repassivation potential are a function of the absolute nitrite concentration or the ratio of nitrite to nitrate.

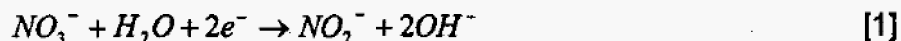
To investigate this, CPP tests were performed in AN107 solutions with different nitrite/nitrate ratios as well as with approximately the same nitrite to nitrate ratio but with different absolute nitrite and nitrate concentrations. Note that the nitrate concentration was 1.5 M when the nitrite/nitrate ratio was 0.5 and 1. The changes of OCP, E_{pit} and E_p at different nitrite/nitrate ratios are plotted in Figure 9.

The trend of OCP, E_{pit} and E_p as a function of nitrite/nitrate ratio is very similar to that was shown in Figure 9, except when the ratio was 0.5 since the solution at this nitrite/nitrate ratio also had a different nitrate concentration (1.5M). This is reasonable because for most tests shown in the nitrate concentration was maintained at 3.7M and thus nitrite concentration was the only variable.

Figure 10 shows the change of E_{pit} , E_p and OCP as a function of nitrite concentration when the ratio of nitrite to nitrate concentration was approximately one. When increasing the nitrite concentration from 1.5M to 3.5M, the values of E_p and E_{pit} remained relatively constant and no significant change in any of the three electrochemical parameters was observed.

Therefore, when the nitrate concentration is fixed, it is beneficial to increase the absolute nitrite concentration. When both nitrite and nitrate concentrations are variable, as is the case for AN107, maintaining a ratio of nitrite to nitrate concentration above 0.5 could be beneficial from a localized corrosion perspective.

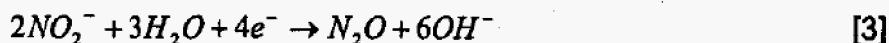
The mechanism of nitrite inhibition for carbon steel localized corrosion in alkaline nitrate solutions is not clear at the present point mainly due to the complexity of the solution chemistry in the tank simulant. In this environment, the high nitrate and nitrite concentrations allow for a range of possible cathodic reactions involving nitrogen-containing species:^{10,11}



$$E_{NO_3^-/NO_2^-}^{rev} = 0.835 - 0.059 pH + 0.0295 \log(NO_3^- / NO_2^-) \quad [1a]$$



$$E_{NO_2^-/NH_3}^{rev} = 0.785 - 0.069 pH + 0.0098 \log[NO_2^-] - 0.0098 \log \alpha_{NH_3} \quad [2a]$$



$$E_{NO_2^-/N_2O}^{rev} = 1.396 - 0.0866 pH + 0.0148 \log([NO_2^-]^2 / p_{N_2O}) \quad [3a]$$

Though these reactions in the tank are likely more complex than those are shown here and have several intermediary steps, they illustrate what several potential cathodic reactions involving nitrogen may be possible. Figure 11 shows a comparison between the reversal potential for the reduction reactions listed above and the OCP as a function of nitrite concentration. The activity of NH_3 and the partial pressure of N_2O were assumed as unity. It can be seen that nitrite concentration had no significant effect on all three reversal potentials. More importantly, the OCP measured in Tank 241-AN-107 simulant solutions was more negative than any of the reversal potentials at any given nitrite concentration. This indicates that all three reactions could contribute to the cathodic reaction at open circuit potential. Therefore, the role of nitrite might be its pH buffer ability by the form of reaction (2) and reaction (3) and thus reduces the corrosivity in the pits. Though no direct measurement or confirmation of these reactions has been performed, they do represent thermodynamically plausible reaction pathways that might explain the beneficial influence of nitrite.

Effect of Total Organic Carbon

To investigate whether the organic carbon compounds function as inhibitors like nitrite, tests were performed in AN107 solutions with different total organic carbon concentrations with and without nitrite.

TOC was found to be a minor inhibitor in the absence of nitrite. The effect of TOC on OCP, E_{pit} and E_{rp} in the absence of nitrite is summarized in FIGURE 12. The values of the three parameters increased slightly with increasing TOC concentration. However, the magnitude of the change was minor. As a matter of fact, E_{rp} remained to be more negative than OCP, indicating that pit initiation is possible. This is a typical behavior in the absence of nitrite and further demonstrated that TOC is not a dominant inhibitor.

In the presence of nitrite, increasing the TOC concentration had a mixed influence on localized corrosion. The effect of TOC on the electrochemical polarization behavior in the presence of nitrite in the AN107 solution is summarized in Figure 13. These data show that TOC had no significant effect on OCP, but did result in some increase in E_{pit} which would generally be considered beneficial. However, an increase in TOC also generally resulted in a decrease in the repassivation potential and tended to move the repassivation potential closer to OCP which is detrimental for localized corrosion resistance. Therefore, it may not be beneficial to include a high concentration of TOC and nitrite at the same time as these two might compete against each other and hence reduce the inhibition effect that can be obtained otherwise from either TOC—albeit minor—or nitrite. Other people also found that some organic compounds at high concentrations could have detrimental effect to pitting corrosion although they were relatively efficient inhibitors at low concentrations¹². Additionally, although the pitting potential in AN107 solution at higher TOC concentration was more positive, the change was not significant and thus it appears that TOC is a weak inhibitor, at best, in AN107 solutions.

Effect of Chloride

It is generally accepted that chloride is detrimental to passive materials and promotes pitting corrosion. Since AN107 solution contains a number of chloride containing species and because carbon steel will tend to be passive in alkaline environments, tests were performed to investigate the effect of chloride on the polarization behavior of carbon steel in AN107 solution. Furthermore, present and endpoint chemistries for Tank 241-AN-107 that contained additional chloride than the standard simulants (0.2M compared to 0.1M) were used to evaluate the impact of chloride on the localized corrosion of other tanks. Three different chloride concentrations, 0.05M, 0.1M and 0.2M, were evaluated, with 0.05 M representing the present chloride concentration in Tank 241-AN-107 and 0.1M being the concentration in the standard AN107 simulant.

In general, chloride only had minor effect on OCP, E_{pit} and E_{rp} of carbon steel in the waste simulant although much stronger effects of chloride on E_{rp} were observed in other environment/materials system¹³. The effect of chloride concentration on OCP, E_{pit} and E_{rp} are summarized in Figure 14. The data show that the increase in the chloride concentration from 0.05M to 0.2M had no significant impact on both the pitting potential the repassivation potentials, although it is generally agreed that the increase in chloride concentration would decrease the pitting potential but usually has no effect on repassivation potential¹⁴.

Since the chloride concentration in the tank remains relatively constant (0.1 M) with time and the variation is also small (0.05M to 0.2M) between different tanks. The above findings could indicate that the small changes in chloride would not introduce any extra risk to the tank materials from the perspective of localized corrosion.

CONCLUSIONS

- ❖ The changes in pH had relatively large impact on the electrochemical polarization behavior when pH was below 10. The difference between the repassivation potential and the corrosion potential was greater than 200 mV at pH values above 10, indicating that pitting corrosion is not likely to occur in the standard simulant; below pH 10, the difference was negative, indicating the likelihood of pitting corrosion. Increasing pH from 11 to 13 or above did not reduce the corrosivity of the simulant considerably.
- ❖ Nitrite served as a potent inhibitor for carbon steel in the environment of interest. A critical concentration at 1.2M or even lower could be beneficial with respect of inhibiting pitting corrosion.
- ❖ The effect of nitrite/nitrate concentration ratio on pitting corrosion was not exactly clear. Based on the experiments been performed, nitrite/nitrate concentration ratios between 0.5 and 1.0 were found to impart substantial resistance to pitting.
- ❖ Organic compounds were weak inhibitors in the absence of nitrite. In the presence of nitrite, high concentration of organic compounds could be detrimental to pitting corrosion of carbon steel as they might reduce the efficiency of other inhibitors (e.g., nitrite).

- ❖ Changing chloride from 0.05M to 0.2M had no significant impact on the localized corrosion of carbon steel in the environment of interest.

Table 1
Summary of main constituents in the waste simulants

Solution Designation	Main Constituents			
	Nitrate (M)	Nitrite (M)	Chloride (M)	pH
Standard Tank 241-AN-107	3.7	1.2	0.1	11
Endpoint Tank 241-AN-107	2.4	2.3	0.1	10
Double Chloride Tank 241-AN-107/Present AN102	3.7	1.2	0.2	11
Double Chloride Endpoint 107/Endpoint AN102	2.4	2.3	0.2	10

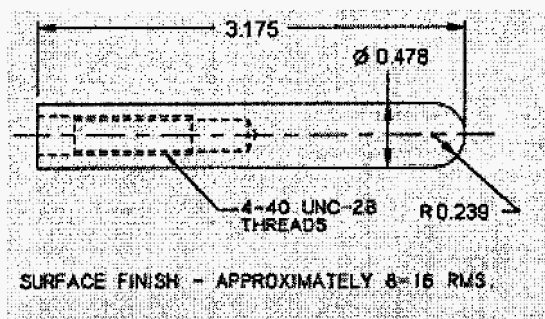


Figure 1-Engineering drawing of the specimen for cyclic potentiodynamic polarization tests (units in cm)

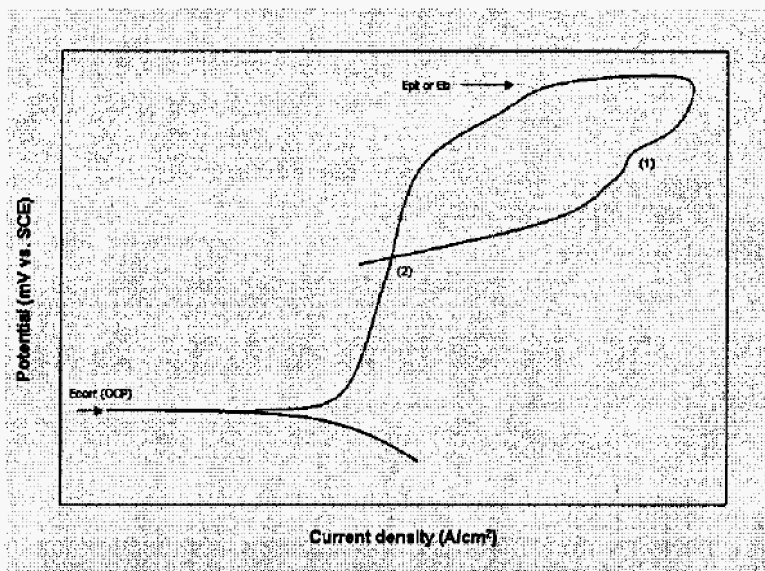


Figure 2-Schematic drawing of typical CPP curve showing pitting potential and two possible repassivation potentials (location (1) and (2)).

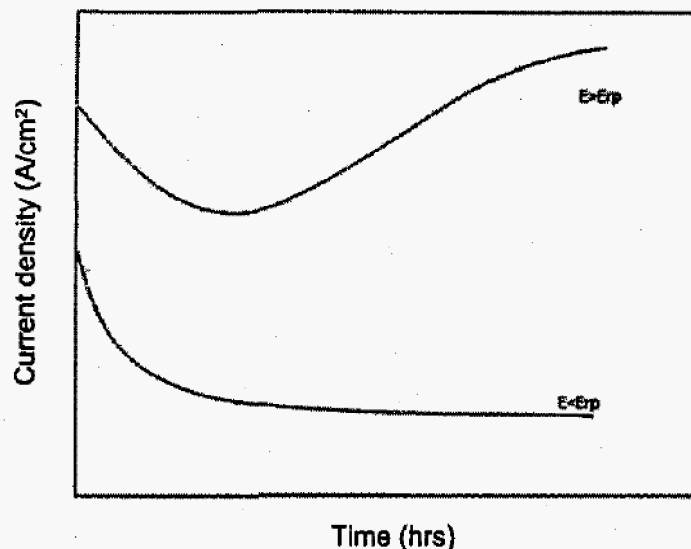


Figure 3-Schematic drawing showing the change of current density as a function of time at potentials higher and lower than E_{rp} , respectively.

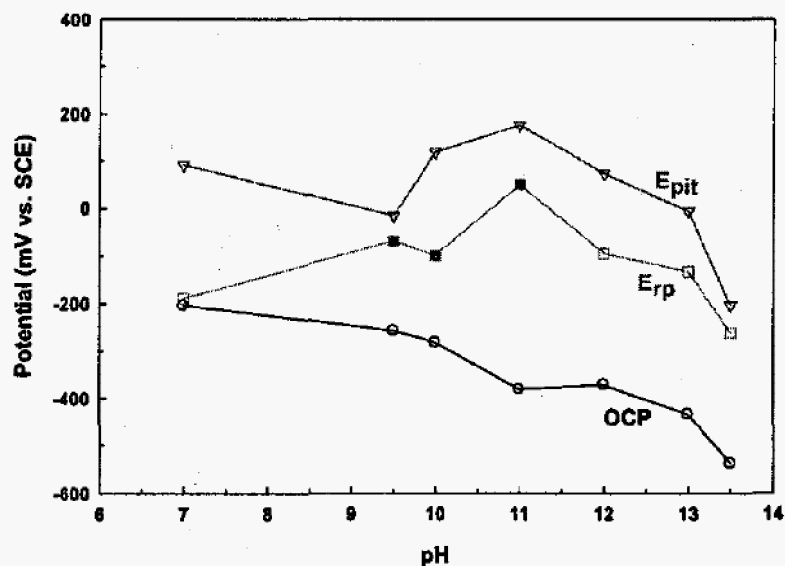


Figure 4-The effect of pH on OCP, E_{pit} and E_{rp} in AN107 solution at different pH values with the same nitrite, nitrate and TOC concentrations ($[NO_2] = 1.2$ M; $[NO_3] = 3.7$ M; TOC=20 g/L). The filled symbols represent the potential obtained from potentiostatic tests.

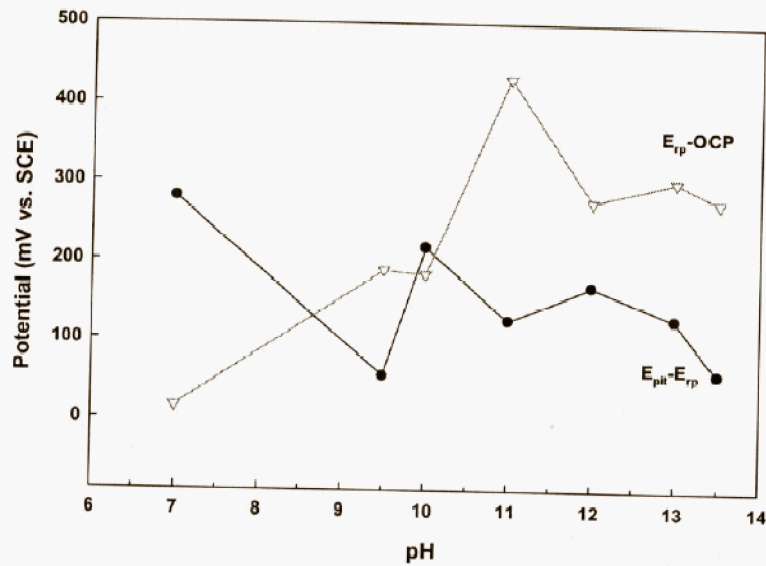


Figure 5-The difference of E_{rp} and OCP ($E_{rp}-OCP$), E_{pit} and E_{rp} ($E_{pit}-E_{rp}$) as a function of pH in AN107 solution.

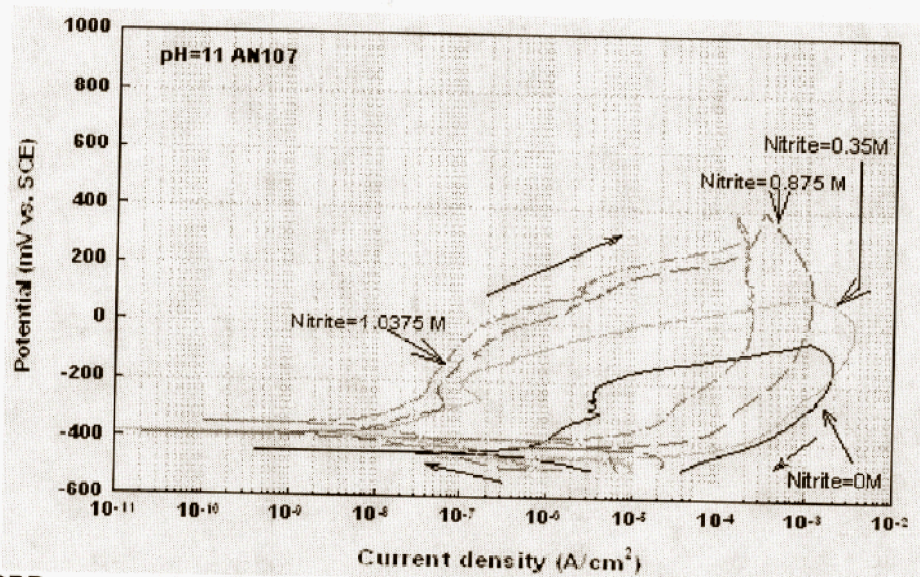


Figure 6-The CPP curves in AN107 solution at pH 11 with different nitrite concentrations

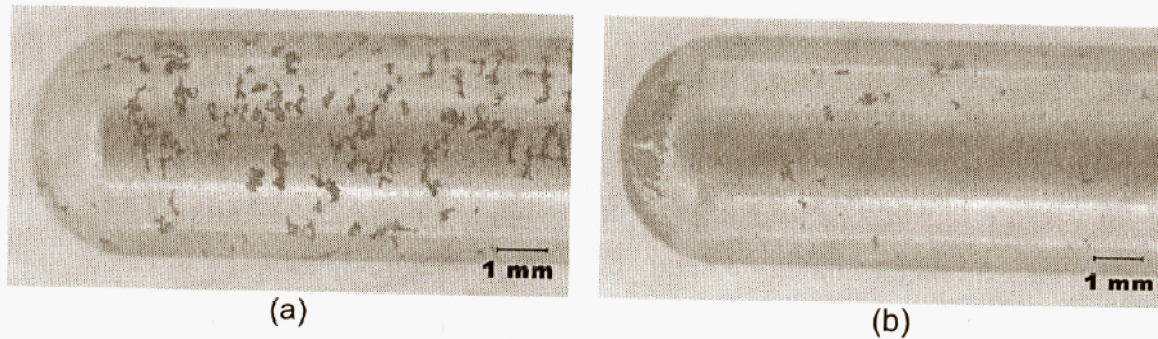


Figure 7-The comparison of the specimen appearance after CPP test at different nitrite concentrations. (a) $[NO_2]=0M$; (b) $[NO_2]=1.2M$

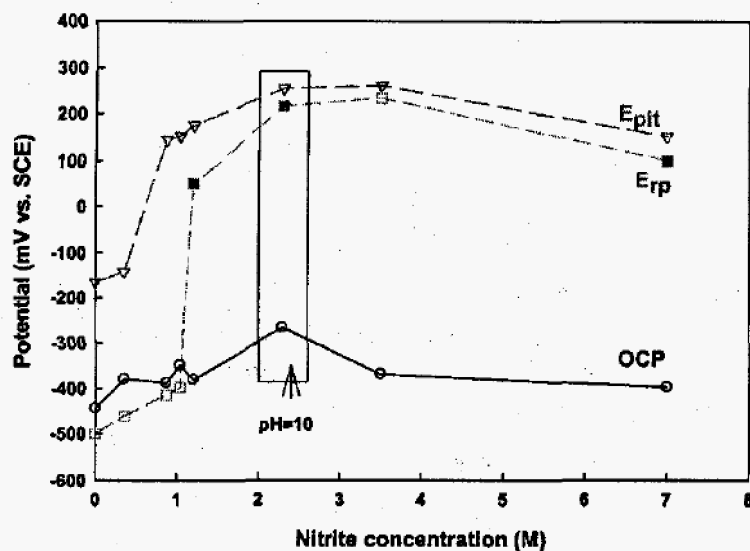


Figure 8-The effect of nitrite concentration on E_{rp} , E_{pit} and OCP. The potentials at 2.3M nitrite are from the CPP test in the endpoint solution at pH 10. All others are from CPP tests in solutions with pH 11. The filled symbols correspond to the values determined from potentiostatic tests.

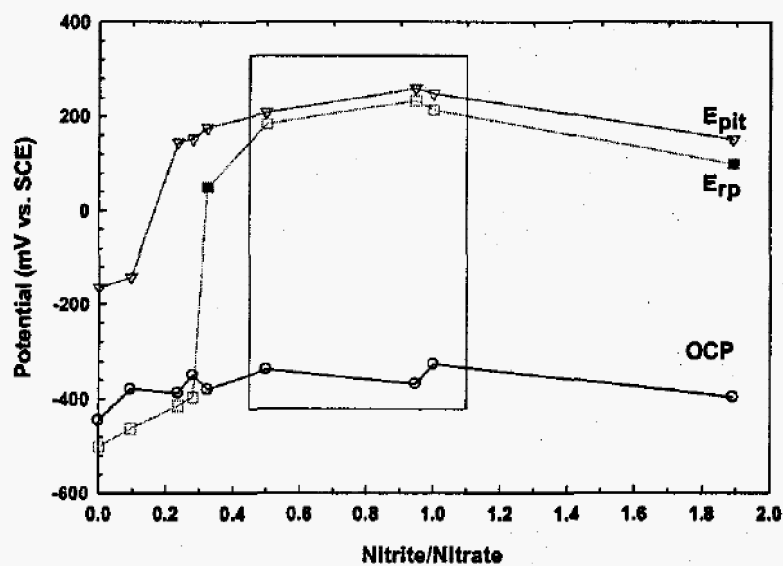


Figure 9-The effect of Nitrite/Nitrate ratio on OCP, E_{pit} and E_{rp} at different nitrite to nitrate ratios (TOC=20 g/L). The filled symbols correspond to the repassivation potentials determined from potentiostatic tests.

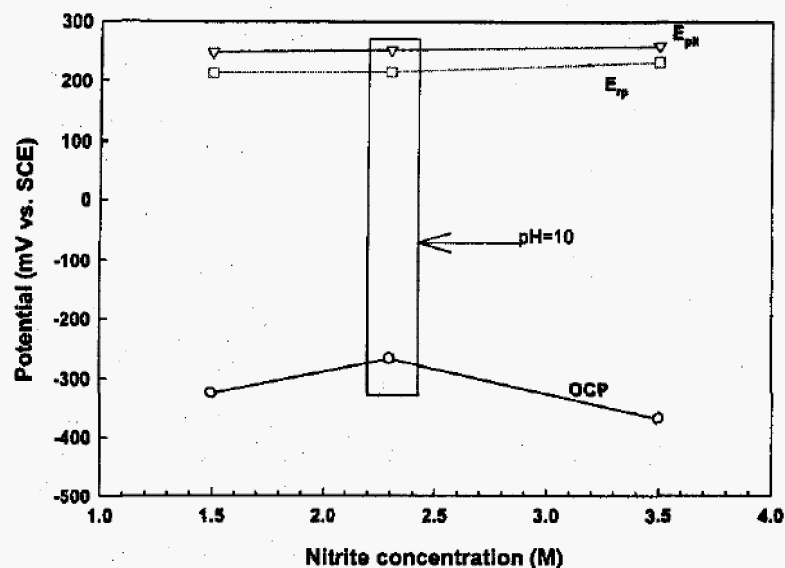


Figure 10-The change of E_{pit} , E_{rp} and OCP as a function of nitrite concentration in AN107 solution when the ratio of nitrite to nitrate is approximately one. The potentials at nitrite concentration of 2.3 M were obtained for AN107 endpoint solution at pH 10. Other values were for Tank 241-AN-107 standard solution at pH 11. The filled symbols correspond to the repassivation potentials determined from potentiostatic tests.

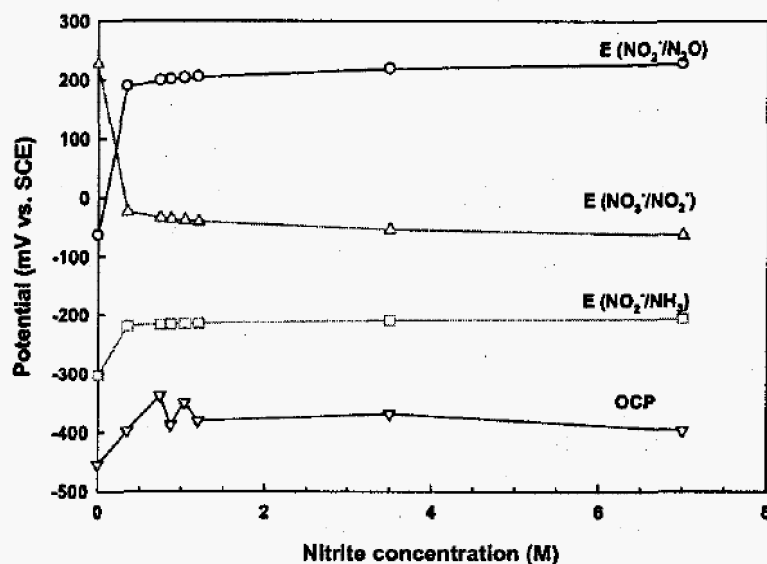


Figure 11-A comparison of reversal potential for different reduction reactions and the OCP in AN107 solution at pH 11. The reversal potentials were calculated with pH 11 and nitrate concentration of 3.7 M.

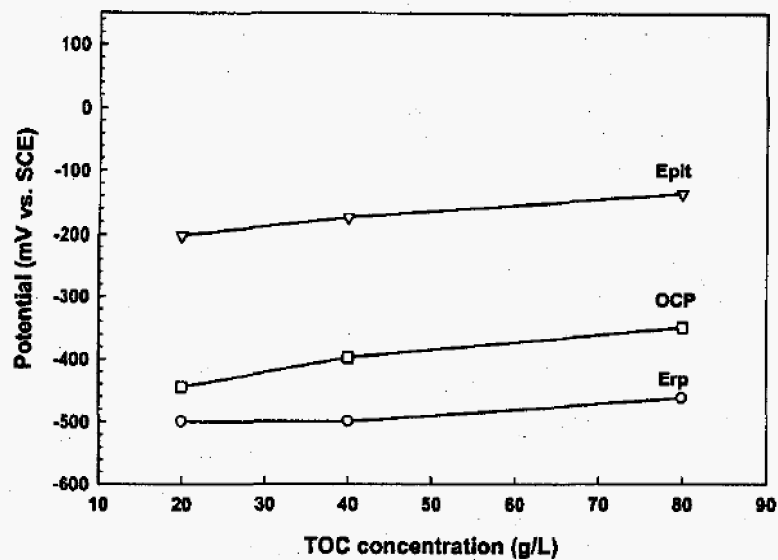


Figure 12-The effect of TOC concentration on OCP, E_{plt} and E_{rp} in AN107 solution in the absence of nitrite.

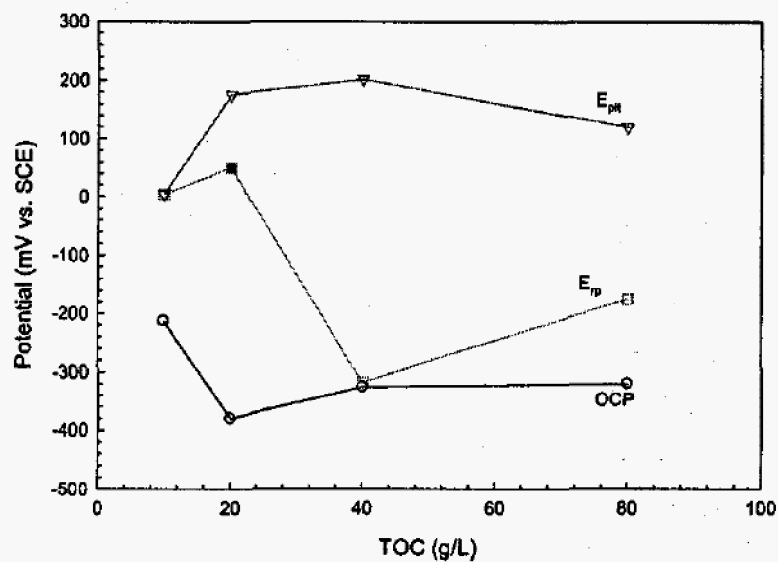


Figure 13-The effect of TOC concentration on OCP, E_{plt} and E_{rp} when nitrite concentration is 1.2M in AN107 solution. The filled symbol at 20 g/L TOC corresponds to the potential value determined from potentiostatic test.

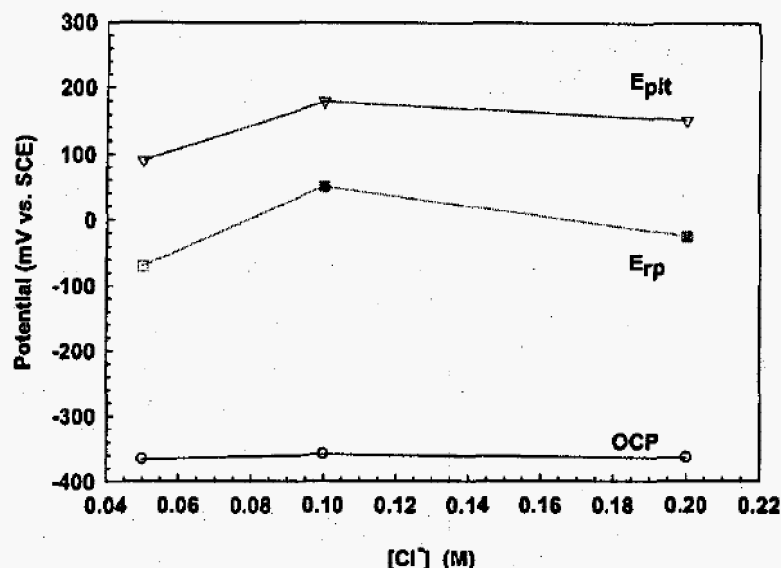


Figure 14-The effect of chloride concentration on OCP, E_{pit} and E_{rp} . The filled symbols correspond to values determined from potentiostatic test.

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